John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 8
Thermochemistry: Chemical Energy

Lecture Notes

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Energy and Its Conservation

Energy: The capacity to supply heat or do work.

Kinetic Energy (E_K): The energy of motion.

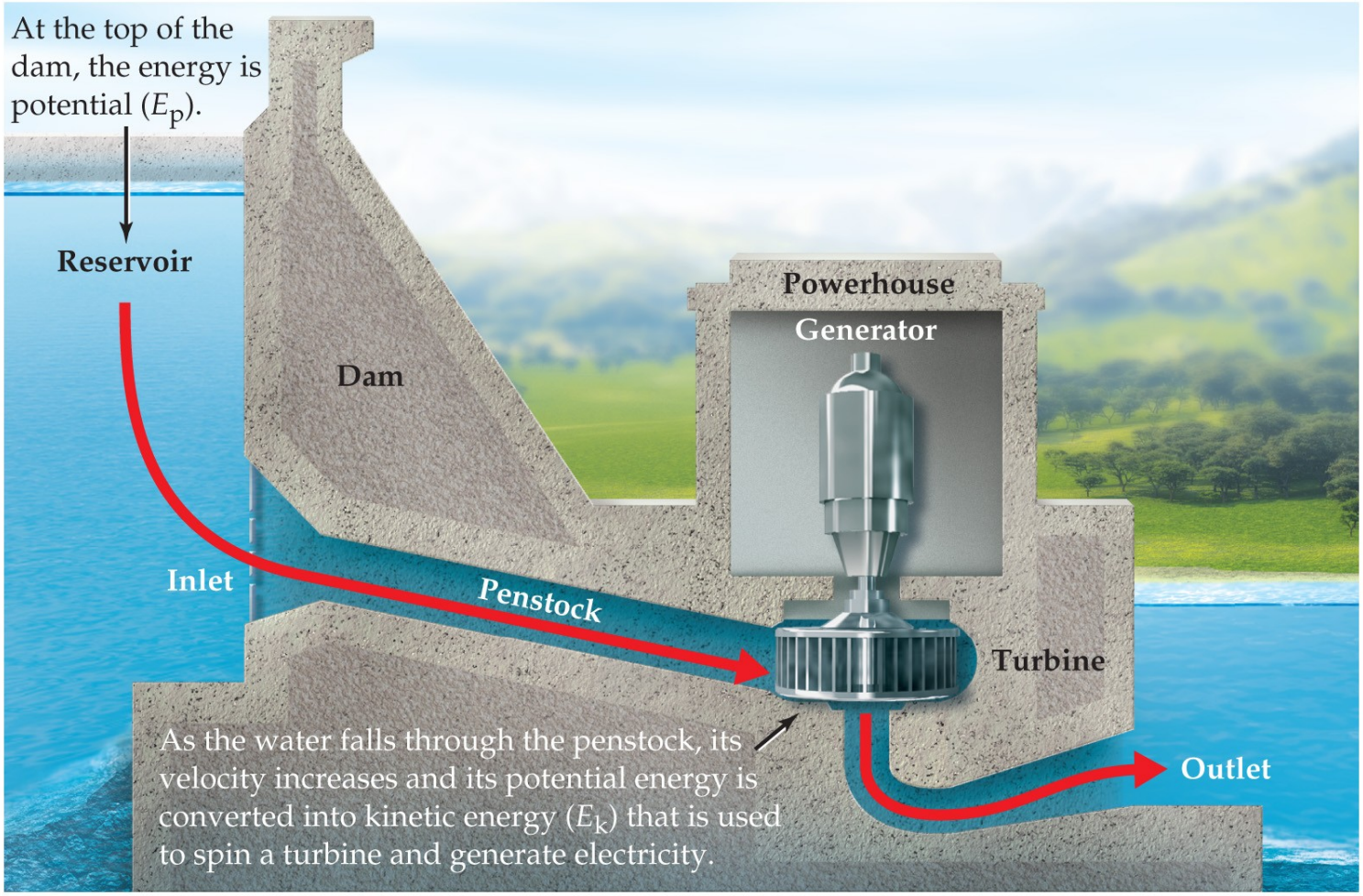
Potential Energy (E_P): Stored energy.

Energy and Its Conservation

Law of Conservation of Energy: Energy cannot be created or destroyed; it can only be converted from one form to another.

Energy and Its Conservation

Total Energy = $E_K + E_P$


At the top of the dam, the energy is potential (E_p).
Reservoir
Dam
Powerhouse
Generator
Inlet
Penstock
Turbine
Outlet
As the water falls through the penstock, its velocity increases and its potential energy is converted into kinetic energy (E_k) that is used to spin a turbine and generate electricity.

Energy and Its Conservation

Thermal Energy: The kinetic energy of molecular motion, measured by finding the *temperature* of an object.

Heat: The amount of thermal energy transferred from one object to another as the result of a *temperature difference* between the two.

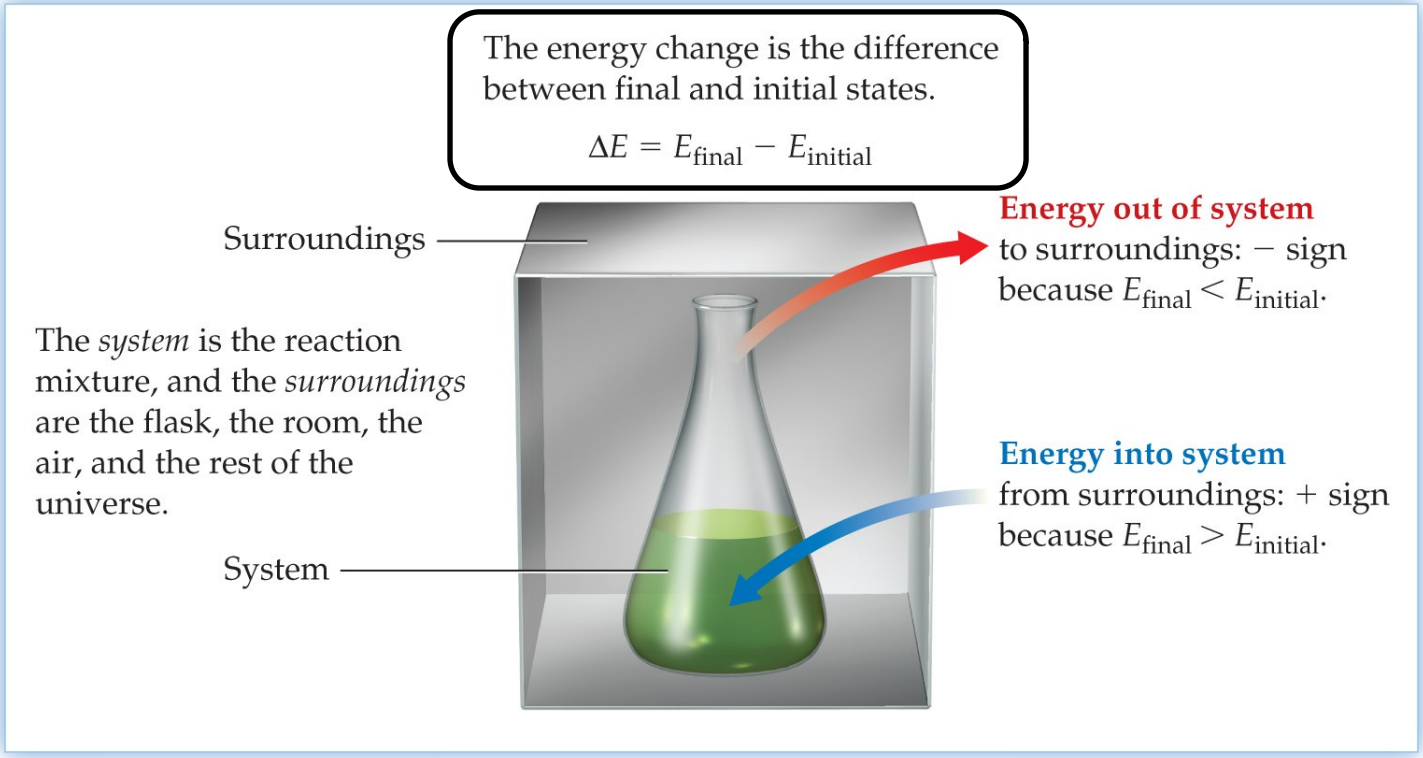
Energy and Its Conservation

First Law of Thermodynamics: Energy cannot be created or destroyed; it can only be converted from one form to another.

Internal Energy and State Functions

First Law of Thermodynamics: The total internal energy of an isolated system is constant.

$$\Delta E = E_{final} - E_{initial}$$



Internal Energy and State Functions

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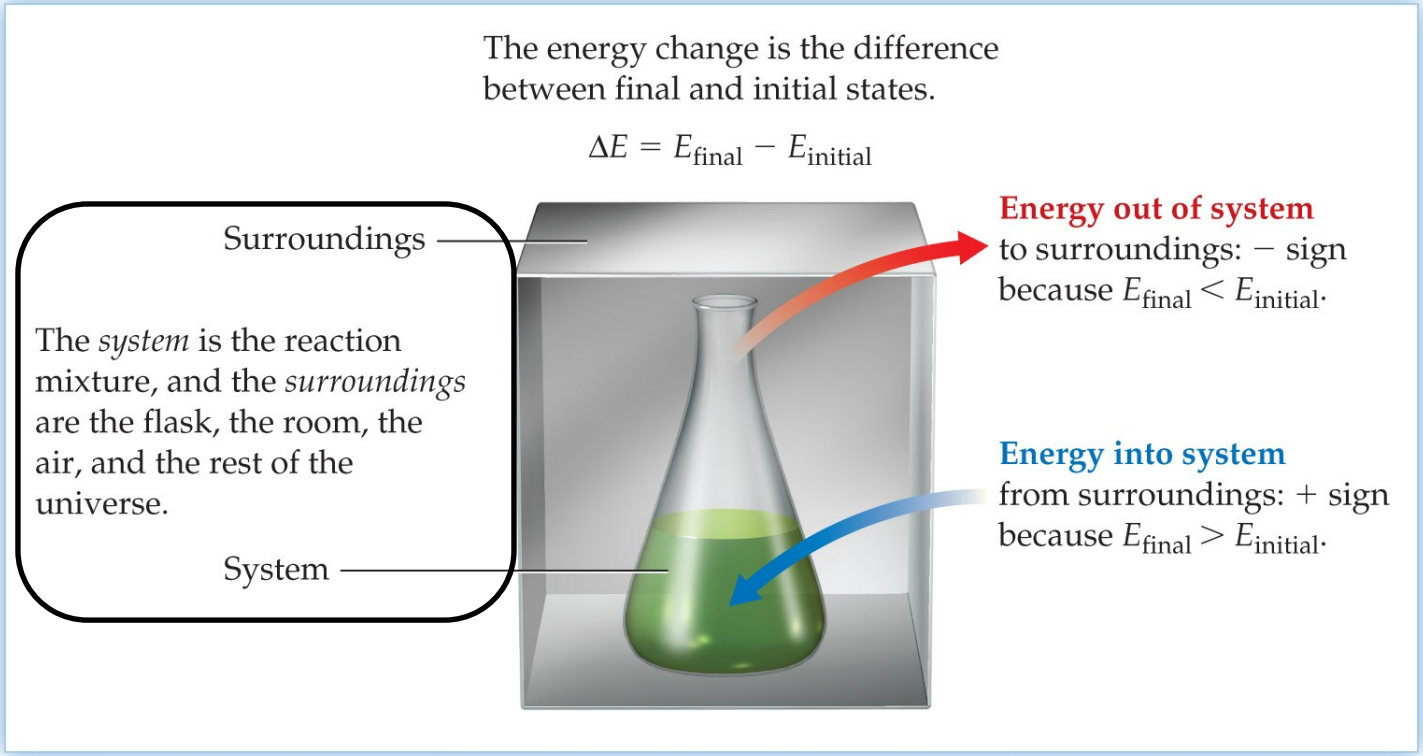

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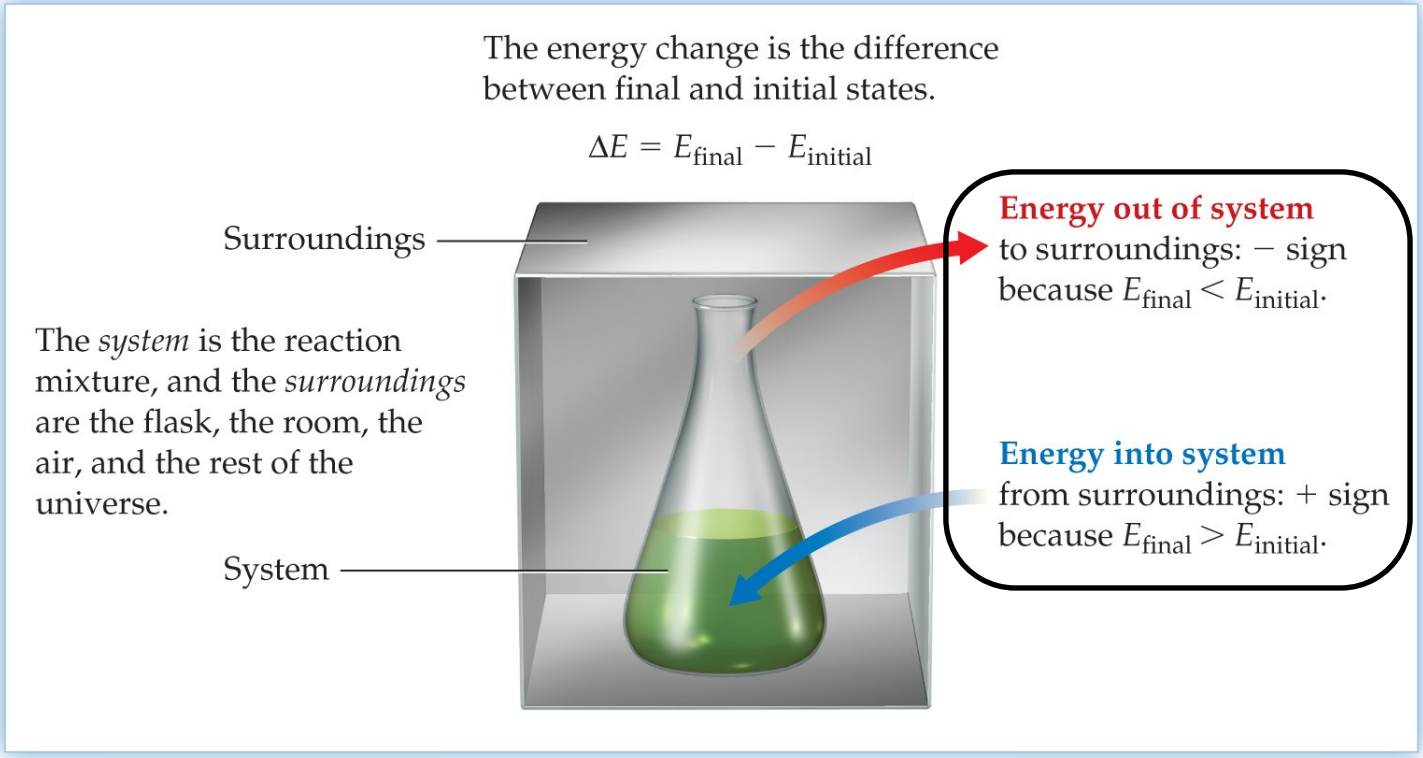


Internal Energy and State Functions

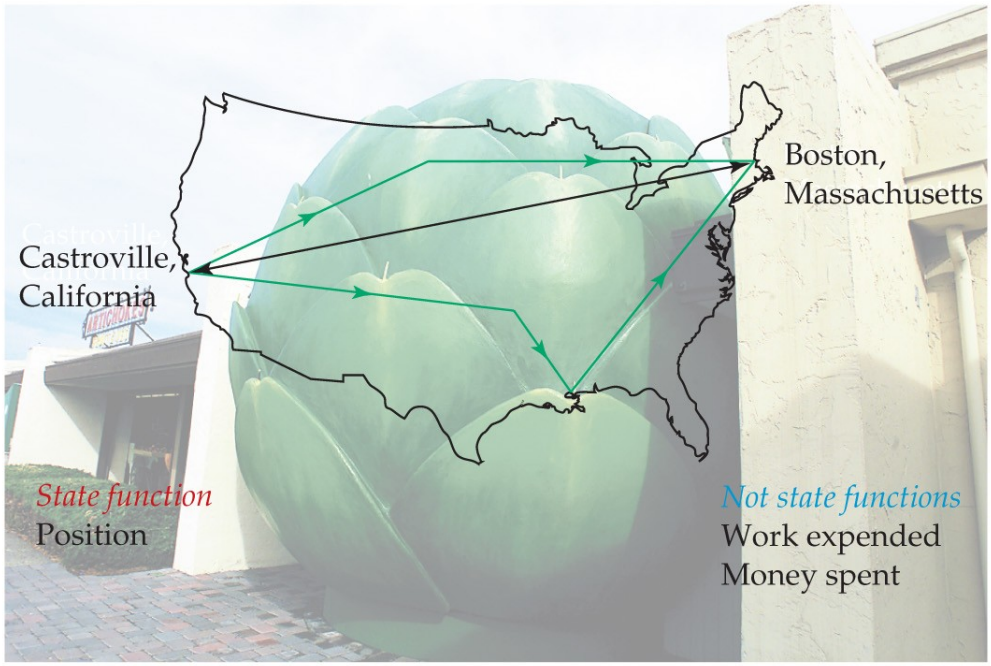
$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) +$ 802 kJ energy

$$\Delta E = E_{final} - E_{initial} = -802 \text{ kJ}$$

802 kJ is released when 1 mole of methane, CH_4, reacts with 2 moles of oxygen to produce 1 mole of carbon dioxide and two moles of water.

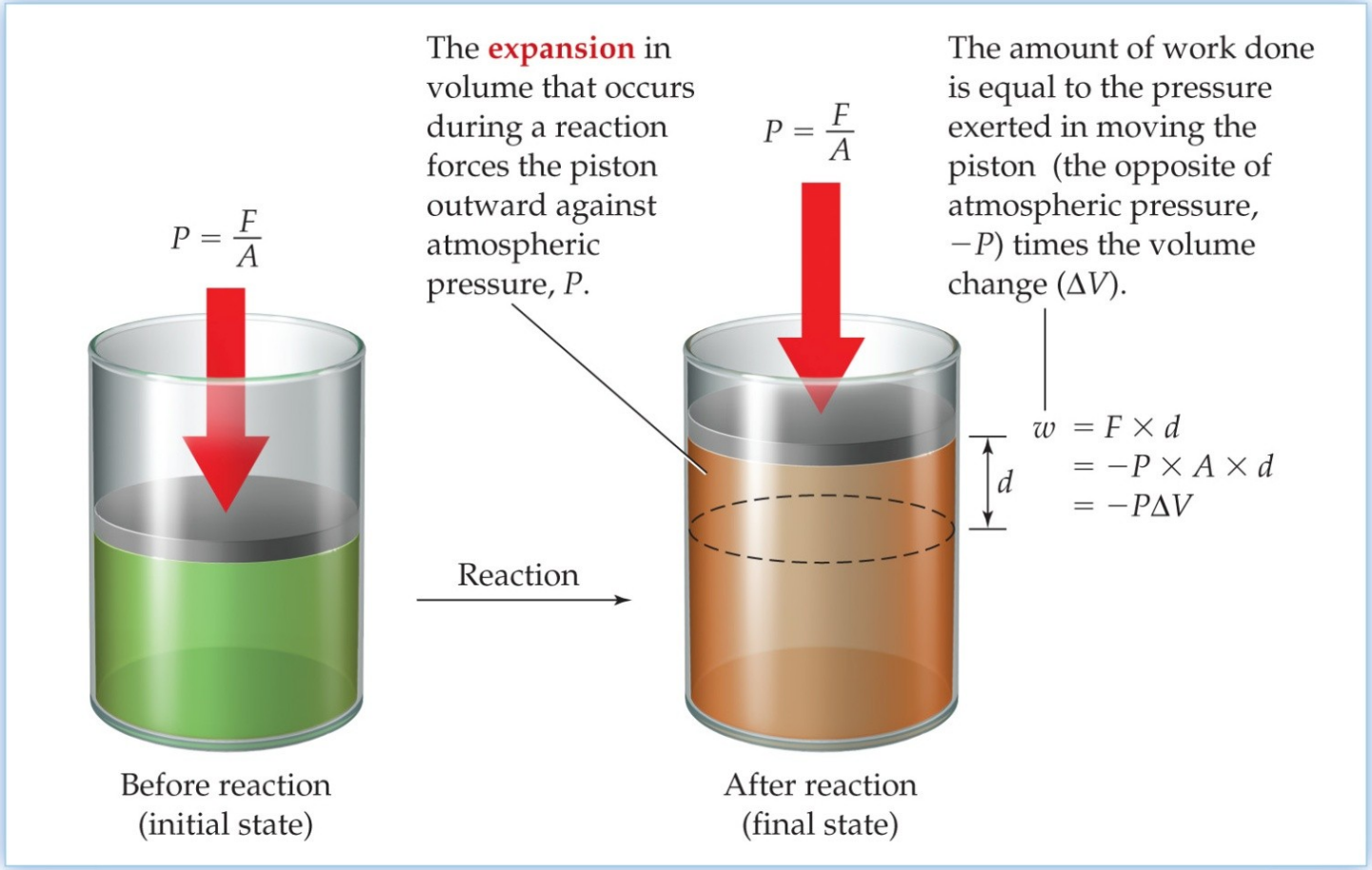
Internal Energy and State Functions

State Function: A function or property whose value depends only on the present state, or condition, of the system, not on the path used to arrive at that state.



Expansion Work

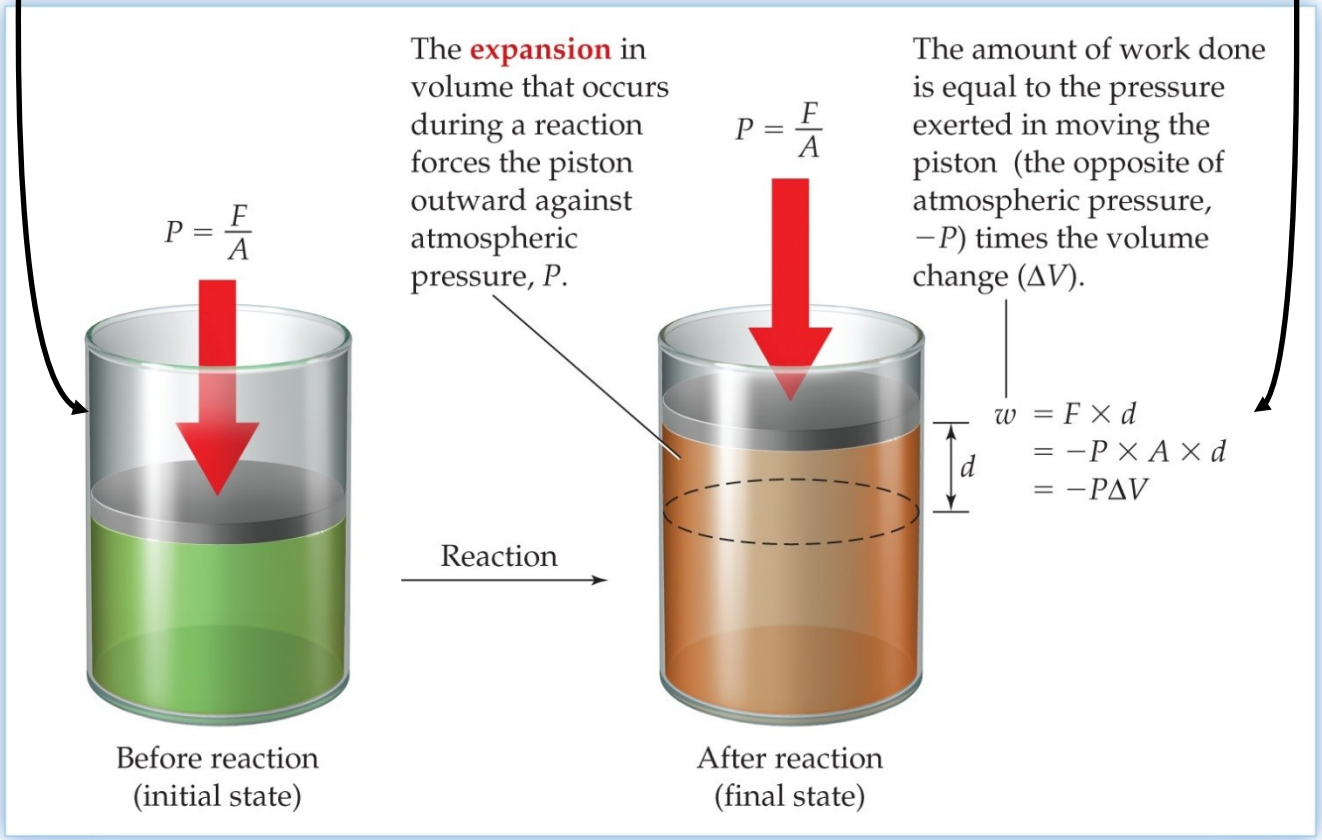
Work = Force x Distance $w = F \times d$


The expansion in volume that occurs during a reaction forces the piston outward against atmospheric pressure, P.
The amount of work done is equal to the pressure exerted in moving the piston (the opposite of atmospheric pressure, −P) times the volume change (ΔV).
$P = \frac{F}{A}$
$P = \frac{F}{A}$
$w = F \times d$
$= -P \times A \times d$
$= -P\Delta V$
d
Reaction
Before reaction
(initial state)
After reaction
(final state)

Expansion Work

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

6 mol of gas → 7 mol of gas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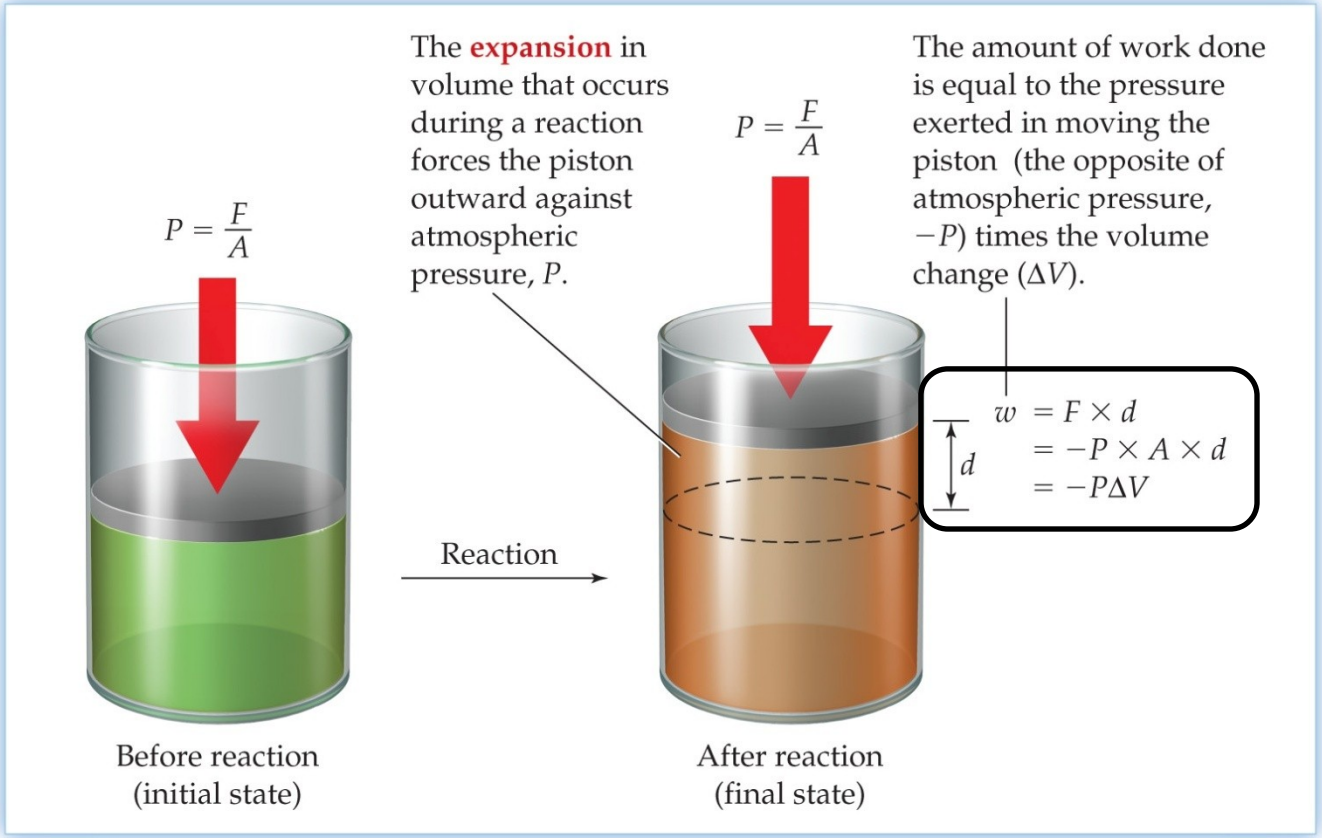
$P = \frac{F}{A}$
$P = \frac{F}{A}$
$w = F \times d$
$= -P \times A \times d$
$= -P\Delta V$
d
Reaction
Before reaction
(initial state)
After reaction
(final state)

Expansion Work

Expansion Work: Work done as the result of a volume change in the system. Also called *pressure-volume* or *PV work*.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$P = \frac{F}{A}$
$P = \frac{F}{A}$
$w = F \times d$
$= -P \times A \times d$
$= -P\Delta V$
d
Reaction
Before reaction
(initial state)
After reaction
(final state)

Energy and Enthalpy

$$\Delta E = q + w$$

q = heat transferred w = work = $-P\Delta V$

$$q = \Delta E + P\Delta V$$

Constant Volume ($\Delta V = 0$): $q_V = \Delta E$

Constant Pressure: $q_P = \Delta E + P\Delta V$

Energy and Enthalpy

$$q_P = \Delta E + P\Delta V = \Delta H$$

Enthalpy change
or
Heat of reaction (at constant pressure

Enthalpy is a state function whose value depends only on the current state of the system, not on the path taken to arrive at that state.

$$\Delta H = H_{final} - H_{initial}$$

$$= H_{products} - H_{reactants}$$

The Thermodynamic Standard State

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta H = -2044$ kJ

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2220$ kJ

Thermodynamic Standard State: Most stable form of a substance at 1 atm pressure and at a specified temperature, usually 25 °C; 1 M concentration for all substances in solution.

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta H° = -2044$ kJ

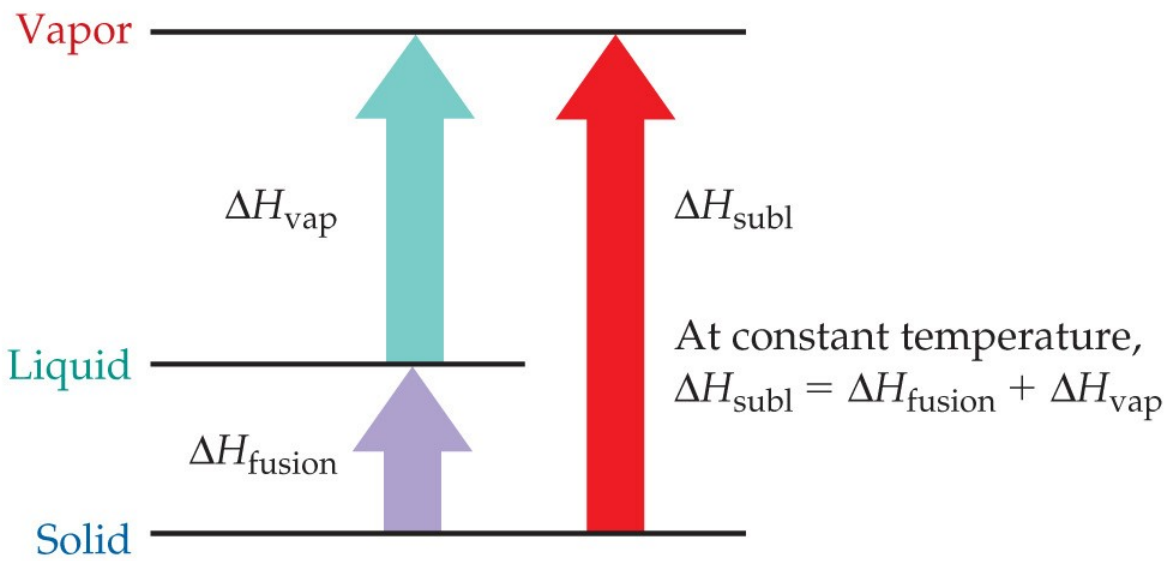
Enthalpies of Physical and Chemical Change

Enthalpy of Fusion (ΔH_{fusion}): The amount of heat necessary to melt a substance without changing its temperature.

Enthalpy of Vaporization (ΔH_{vap}): The amount of heat required to vaporize a substance without changing its temperature.

Enthalpy of Sublimation (ΔH_{subl}): The amount of heat required to convert a substance from a solid to a gas without going through a liquid phase.

Enthalpies of Physical and Chemical Change



Enthalpies of Physical and Chemical Change

$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s) \quad \Delta H° = -852\ kJ$

Exothermic: Heat (enthalpy) flows from the system to the surroundings.

$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \longrightarrow$

$BaCl_2(aq) + 2NH_3(aq) + 10H_2O(l) \quad \Delta H° = +80.3\ kJ$

Endothermic: Heat (enthalpy) flows from the surroundings to the system.

Enthalpies of Physical and Chemical Change

$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s) \quad \Delta H° = -852\ kJ$

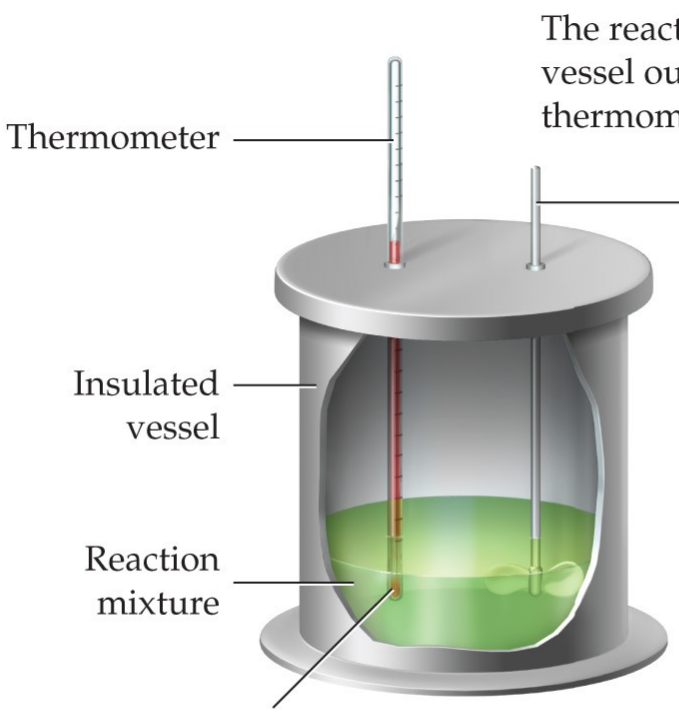
Exothermic: Heat (enthalpy) flows from the system to the surroundings.

$2Fe(s) + Al_2O_3(s) \longrightarrow 2Al(s) + Fe_2O_3(s) \quad \Delta H° = +852\ kJ$

Endothermic: Heat (enthalpy) flows from the surroundings to the system.

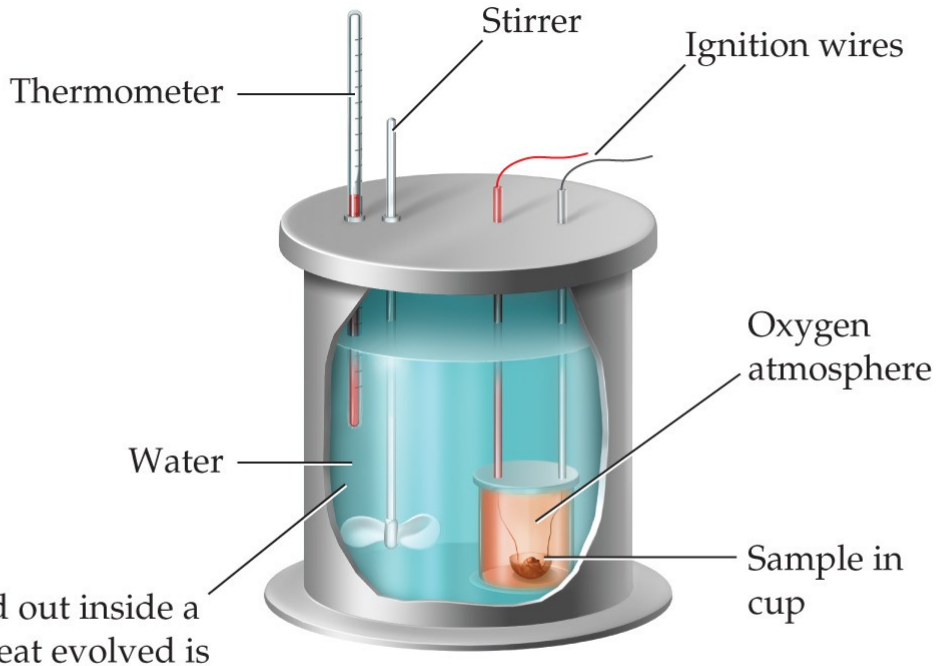
Calorimetry and Heat Capacity

Measure the heat flow at *constant pressure* (**Δ*H***).


The reaction takes place inside an insulated vessel outfitted with a loose-fitting top, a thermometer, and a stirrer.
Thermometer
Stirrer
Insulated vessel
Reaction mixture
Measuring the temperature change that accompanies the reaction makes it possible to calculate ΔH.

Calorimetry and Heat Capacity

Measure the heat flow at *constant volume* (**Δ*E***).



The reaction is carried out inside a steel bomb, and the heat evolved is transferred to the surrounding water, where the temperature rise is measured.

Calorimetry and Heat Capacity

Heat Capacity (*C*): The amount of heat required to raise the temperature of an object or substance a given amount.

$$q = C \times \Delta T$$

Molar Heat Capacity (C_m): The amount of heat required to raise the temperature of 1 mol of a substance by 1 °C.

$$q = (C_m) \times (\text{moles of substance}) \times \Delta T$$

Specific Heat: The amount of heat required to raise the temperature of 1 g of a substance by 1 °C.

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times \Delta T$$

Calorimetry and Heat Capacity

TABLE 8.1 Specific Heats and Molar Heat Capacities for Some Common Substances at 25 °C

Substance	Specific Heat J/(g · °C)	Molar Heat Capacity J/(mol · °C)
Air (dry)	1.01	29.1
Aluminum	0.897	24.2
Copper	0.385	24.4
Gold	0.129	25.4
Iron	0.449	25.1
Mercury	0.140	28.0
NaCl	0.859	50.2
Water(*s*)*	2.03	36.6
Water(*l*)	4.179	75.3

*At −11 °C

Calorimetry and Heat Capacity

Assuming that a can of soda has the same specific heat as water, calculate the amount of heat (in kilojoules) transferred when one can (about 350 g) is cooled from 25 °C to 3 °C.

q = (specific heat) x (mass of substance) x ΔT

Specific heat = $4.18 \frac{\text{J}}{\text{g °C}}$

Mass = 350 g

Temperature change = 25 °C - 3 °C = 22 °C

Calorimetry and Heat Capacity

Calculate the amount of heat transferred.

$$\text{Heat evolved} = \frac{4.18\ \text{J}}{\text{g}\ ^\circ\text{C}} \times 350\ \text{g} \times 22\ ^\circ\text{C} = 32\,000\ \text{J}$$

$$32\,000\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = \boxed{32\ \text{kJ}}$$

Hess's Law

Hess's Law: The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction.

Haber Process $3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$ $\Delta H° = -92.2$ kJ

Multiple-Step Process

$2H_2(g) + N_2(g) \longrightarrow \cancel{N_2H_4(g)}$ $\Delta H°_1 = ?$

$\cancel{N_2H_4(g)} + H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H°_2 = -187.6$ kJ

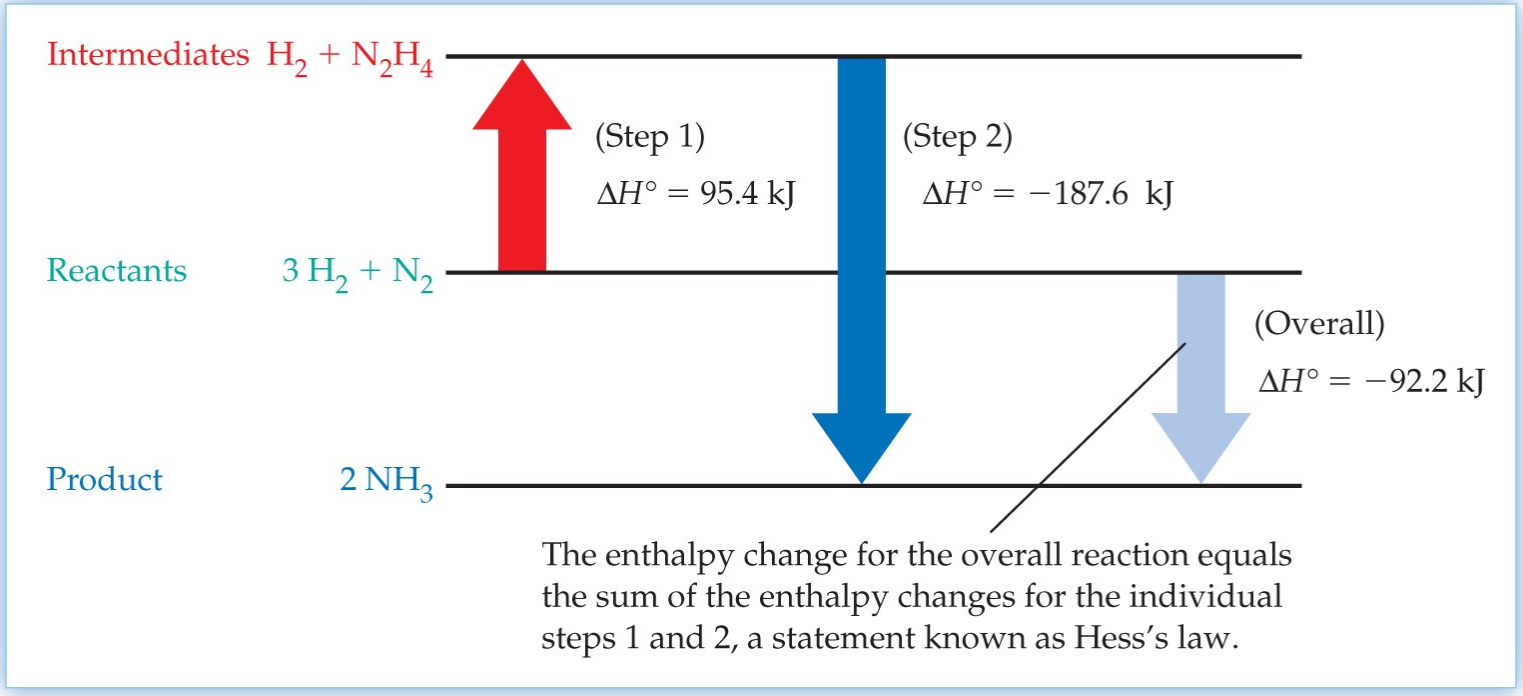
$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$ $\Delta H°_{1+2} = -92.2$ kJ

Hess's Law

$$\Delta H^\circ_1 + \Delta H^\circ_2 = \Delta H^\circ_{1+2}$$

$$\Delta H^\circ_1 = \Delta H^\circ_{1+2} - \Delta H^\circ_2$$

$$= -92.2 \text{ kJ} - (-187.6 \text{ kJ}) = 95.4 \text{ kJ}$$


Intermediates $H_2 + N_2H_4$
Reactants $3\,H_2 + N_2$
Product $2\,NH_3$
(Step 1)
$\Delta H^\circ = 95.4$ kJ
(Step 2)
$\Delta H^\circ = -187.6$ kJ
(Overall)
$\Delta H^\circ = -92.2$ kJ
The enthalpy change for the overall reaction equals the sum of the enthalpy changes for the individual steps 1 and 2, a statement known as Hess's law.

Standard Heats of Formation

Standard Heat of Formation (ΔH°_f): The enthalpy change for the formation of 1 mol of a substance in its standard state from its constituent elements in their standard states.

Standard states

$$\overbrace{C(s) + 2H_2(g)} \longrightarrow \underbrace{CH_4(g)} \quad \Delta H^\circ_f = -74.8 \text{ kJ}$$

1 mol of 1 substance

Standard Heats of Formation

TABLE 8.2 Standard Heats of Formation for Some Common Substances at 25 °C

Substance	Formula	ΔH°_f (kJ/mol)	Substance	Formula	ΔH°_f (kJ/mol)
Acetylene	$C_2H_2(g)$	227.4	Hydrogen chloride	$HCl(g)$	−92.3
Ammonia	$NH_3(g)$	−46.1	Iron(III) oxide	$Fe_2O_3(s)$	−824.2
Carbon dioxide	$CO_2(g)$	−393.5	Magnesium carbonate	$MgCO_3(s)$	−1095.8
Carbon monoxide	$CO(g)$	−110.5	Methane	$CH_4(g)$	−74.8
Ethanol	$C_2H_5OH(l)$	−277.7	Nitric oxide	$NO(g)$	91.3
Ethylene	$C_2H_4(g)$	52.3	Water (g)	$H_2O(g)$	−241.8
Glucose	$C_6H_{12}O_6(s)$	−1273.3	Water (l)	$H_2O(l)$	−285.8

Standard Heats of Formation

$$\Delta H^\circ = \Delta H^\circ_f \text{ (Products)} - \Delta H^\circ_f \text{ (Reactants)}$$

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

$$\Delta H^\circ = \underbrace{[c\,\Delta H^\circ_f \text{ (C)} + d\,\Delta H^\circ_f \text{ (D)}]}_{\text{Products}} - \underbrace{[a\,\Delta H^\circ_f \text{ (A)} + b\,\Delta H^\circ_f \text{ (B)}]}_{\text{Reactants}}$$

Standard Heats of Formation

Using standard heats of formation, calculate the standard enthalpy of reaction for the photosynthesis of glucose ($C_6H_{12}O_6$) and O_2 from CO_2 and liquid H_2O.

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H^\circ = ?$$

$$H^\circ = [\Delta H^\circ_f (C_6H_{12}O_6(s))] - [6\ \Delta H^\circ_f (CO_2(g)) + 6\ \Delta H^\circ_f (H_2O(l))$$

$$\Delta H^\circ = [(1 \text{ mol})(-1273.3 \text{ kJ/mol})] -$$

$$[(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-285.8 \text{ kJ/mol})$$

$$= \boxed{2802.5 \text{ kJ}}$$

Standard Heats of Formation

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H° = 2802.5 \text{ kJ}$$

(1) (2) (3)

Why does the calculation "work"?

1. Reverse the "reaction" and reverse the sign on the standard enthalpy change.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -393.5 \text{ kJ}$$

Becomes

$$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta H° = 393.5 \text{ kJ}$$

Standard Heats of Formation

$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H° = 2802.5\ kJ$

(1) (2) (3)

Why does the calculation "work"?

1. Multiply the coefficients by a factor and multiply the standard enthalpy change by the same factor.

$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta H° = -393.5\ kJ$

Becomes

$6CO_2(g) \longrightarrow 6C(s) + 6O_2(g) \quad \Delta H° = 6(393.5\ kJ) = 2361.0\ kJ$

Standard Heats of Formation

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H° = 2802.5 \text{ kJ}$$

(1) (2) (3)

Why does the calculation "work"?

2. Reverse the "reaction" and reverse the sign on the standard enthalpy change.

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -285.8 \text{ kJ}$$

Becomes

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g) \quad \Delta H° = 285.8 \text{ kJ}$$

Standard Heats of Formation

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H° = 2802.5 \text{ kJ}$$

(1) (2) (3)

Why does the calculation "work"?

2. Multiply the coefficients by a factor and multiply the standard enthalpy change by the same factor.

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g) \quad \Delta H° = 285.8 \text{ kJ}$$

Becomes

$$6H_2O(l) \longrightarrow 6H_2(g) + 3O_2(g) \quad \Delta H° = 6(285.8 \text{ kJ}) = 1714.8 \text{ kJ}$$

Standard Heats of Formation

$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$ $\Delta H° = 2802.5$ kJ

(1) (2) (3)

Why does the calculation "work"?

~~$6C(s) + 6H_2(g) + 3O_2(g)$~~ $\longrightarrow C_6H_{12}O_6(s)$ $\Delta H° = -1273.3$ kJ

$6CO_2(g) \longrightarrow$ ~~$6C(s)$~~ $+ 6O_2(g)$ $\Delta H° = 2361.0$ kJ

$6H_2O(l) \longrightarrow$ ~~$6H_2(g)$~~ $+$ ~~$3O_2(g)$~~ $\Delta H° = 1714.8$ kJ

$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$

$\Delta H° = 2802.5$ kJ

Bond Dissociation Energies

Bond Dissociation Energy:

- The amount of energy that must be supplied to break a chemical bond in an isolated molecule in the gaseous state and is thus the amount of energy released when the bond forms.

or

- Standard enthalpy changes for the corresponding bond-breaking reactions.

Bond Dissociation Energies

TABLE 5.1 Average Bond Dissociation Energies, *D* (kJ/mol)

H—H	436[a]	C—H	410	N—H	390	O—H	460	F—F	159[a]		
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243[a]		
H—F	570[a]	C—F	450	N—F	270	O—F	180	Br—Br	193[a]		
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151[a]		
H—Br	366[a]	C—Br	270	N—Br	240	O—Br	210	S—F	310		
H—I	298[a]	C—I	240	N—I	—	O—I	220	S—Cl	250		
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210		
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225		
H—S	340	C—S	260	N—S	—	O—S	—				
Multiple covalent bonds[b]											
C=C	728	C≡C	965	C=O	732	O=O	498[a]	N≡N	945[a]		

[a]Exact value.

[b]We'll discuss multiple covalent bonds in Section 5.6.

Bond Dissociation Energies

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

$$\Delta H^\circ = D(\text{Reactant bonds}) - D(\text{Product bonds})$$

$$\Delta H^\circ = (D_{H\text{-}H} + D_{Cl\text{-}Cl}) - (2D_{H\text{-}Cl})$$

$$\Delta H^\circ = [(1\ \text{mol})(436\ \text{kJ/mol}) + (1\text{mol})(243\ \text{kJ/mol})] - (2\text{mol})(432\ \text{kJ/mol})$$

$$= \boxed{-185\ \text{kJ}}$$

Fossil Fuels, Fuel Efficiency, and Heats of Combustion

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H°_c = [\Delta H°_f (CO_2(g)) + 2\ \Delta H°_f (H_2O(l))] - [\Delta H°_f (CH_4(g))]$$

$$= [(1\ \text{mol})(-393.5\ \text{kJ/mol}) + (2\ \text{mol})(-285.8\ \text{kJ/mol})] - [(1\ \text{mol})(-74.8\ \text{kJ/mol})]$$

$$= \boxed{-890.3\ \text{kJ}}$$

Fossil Fuels, Fuel Efficiency, and Heats of Combustion

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

TABLE 8.3 Thermochemical Properties of Some Fuels

Fuel	Combustion Enthalpy		
	kJ/mol	kJ/g	kJ/mL
Hydrogen, $H_2(l)$	−285.8	−141.8	−9.9*
Ethanol, $C_2H_5OH(l)$	−1366.8	−29.7	−23.4
Graphite, $C(s)$	−393.5	−32.8	−73.8
Methane, $CH_4(g)$	−890.3	−55.5	−30.8*
Methanol, $CH_3OH(l)$	−725.9	−22.7	−17.9
Octane, $C_8H_{18}(l)$	−5470	−47.9	−33.6
Toluene, $C_7H_8(l)$	−3910	−42.3	−36.7

*Calculated for the compressed liquid at 0 °C.

An Introduction to Entropy

Spontaneous Process: A process that, once started, proceeds on its own without a continuous external influence.

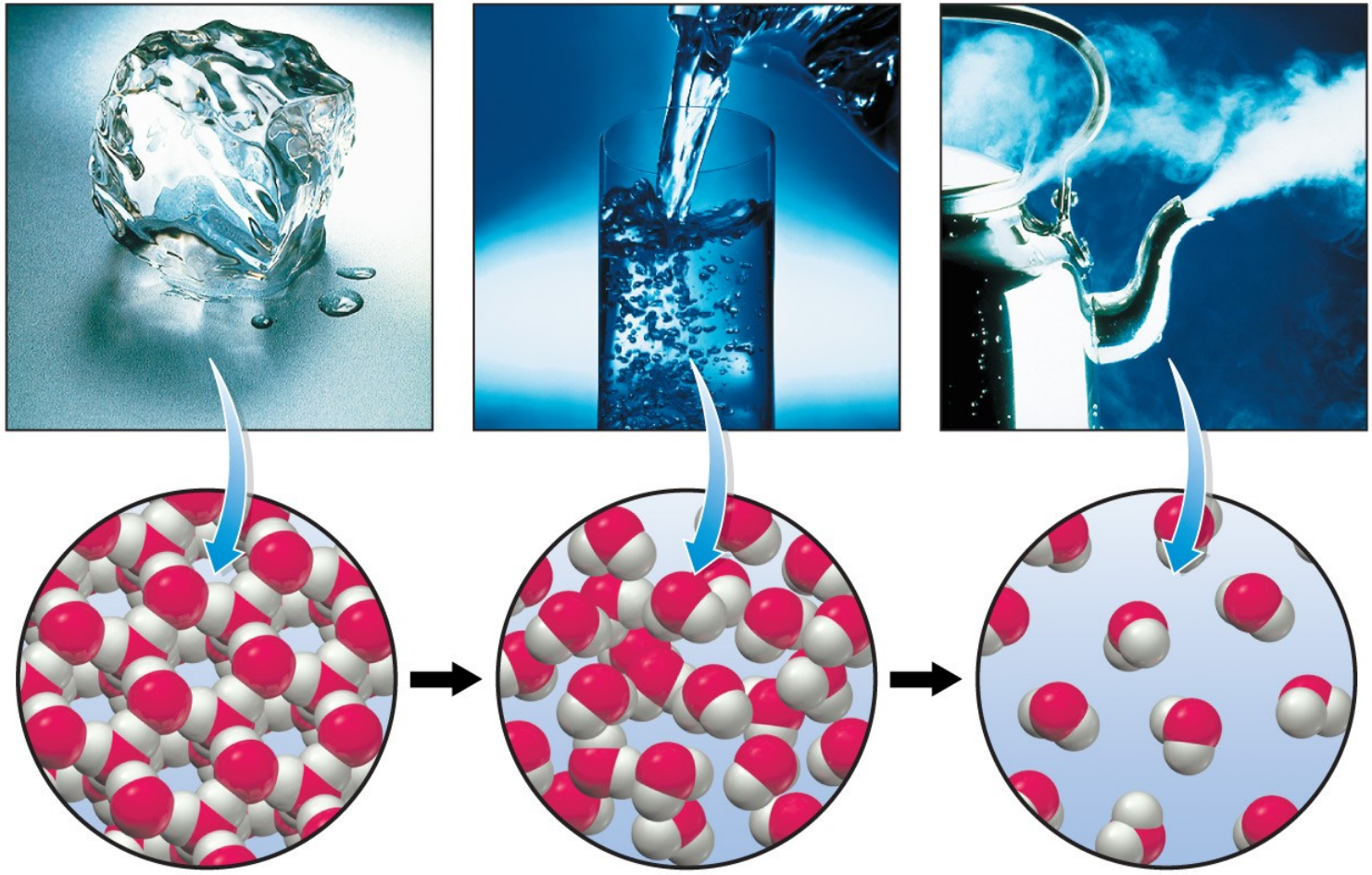
Entropy (*S*): The amount of molecular randomness in a system.

Spontaneous processes are

- favored by a decrease in H (negative ΔH).
- favored by an increase in S (positive ΔS).

Nonspontaneous processes are

- favored by an increase in H (positive ΔH).



Liquids have more randomness and higher entropy than **solids.**

Gases have more randomness and higher entropy than liquids.

Less randomness, lower entropy → More randomness, higher entropy

An Introduction to Free Energy

Gibbs Free Energy Change (ΔG)

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy of reaction

Temperature (Kelvin)

Entropy change

An Introduction to Free Energy

Gibbs Free Energy Change (ΔG)

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G < 0$ Process is spontaneous

$\Delta G = 0$ Process is at equilibrium
(neither spontaneous nor nonspontaneous)

$\Delta G > 0$ Process is nonspontaneous

An Introduction to Free Energy

$\Delta S° = +22.0\ \text{J/(K} \cdot \text{mol)}$ **(Entropy increases)**
$\Delta H° = +6.01\ \text{kJ/mol}$ **(Endothermic)**

Spontaneous above 0 °C

Spontaneous below 0 °C

$\Delta S° = -22.0\ \text{J/(K} \cdot \text{mol)}$ **(Entropy decreases)**
$\Delta H° = -6.01\ \text{kJ/mol}$ **(Exothermic)**

Solid water

Liquid water

Below 0 °C, the enthalpy term ΔH dominates the entropy term $T\Delta S$ in the Gibbs free-energy equation, so freezing is spontaneous.

At 0 °C the entropy and enthalpy terms are exactly balanced.

Above 0 °C, the entropy term dominates the enthalpy term, so melting is spontaneous.